Studies of the Processes Operative in Solutions. XXVIII.—*The Influence of Acids on the Rotatory Power of Cane Sugar, of Glucose and of Fructose.*

By F. P. Worley.

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It is shown in Part XXII of this series of studies that when cane sugar is hydrolysed in the presence of solutions of sulphuric acid of different concentrations, the ratio of the final value of the rotation of the invert sugar to the initial value due to the cane sugar becomes very considerably greater as the concentration of the acid is increased. The effect was attributed to an increase in the optical rotatory power of the sugars caused by the acid; from the fact that the ratio of acid to sugar was the same in most of the experiments, it was argued that the determining factor was the ratio of acid to water, the alteration in the rotatory power being due mainly to changes in the water. Judging from the results of preliminary experiments and the work of previous investigators, it was probable that the fructose was the sugar chiefly affected but that the observed change in the above ratio could not be attributed to this cause alone.

In the course of experiments recently carried out to determine the hydrolytic activity of benzenesulphonic acid at different degrees of dilution, data have been accumulated which confirm the results arrived at when sulphuric acid was used as the hydrolyst. Experiments have also been carried out to determine the effect of the acid on the rotatory power of cane sugar, glucose and fructose.

It will be seen on reference to the following table that as the concentration of the acid is increased from one molecular proportion in two hundred of

Table I.

Mol. prop. of cane sugar.	Mol. prop. of hydrone.	Initial rotation.	Final rotation.	Ratio of final to initial rotation.
0·125	30	+ 9°·78	−3°·44	0·352
0·25	40	14°·92	4°·99	0·334
0·25	50	12°·43	4°·07	0·326
0·25	60	10°·68	3°·43	0·322
0·25	80	16°·60	5°·18	0·312
0·25	100	13°·52	4°·15	0·306
0·5	200	13°·98	4°·16	0·298

(Observations were made in the light of the mercury green line.)

"hydrone" (H_2O) to one in thirty, the ratio of the final negative rotation to the initial positive rotation is increased by about 17 per cent. In the experiments with from 30 to 60 molecular proportions of hydrone, polarimeter tubes two decimetres long were used and in the others tubes four decimetres long. One molecular proportion of acid was used throughout.

The results are set forth graphically in Diagram I. The values of the ratio of the final negative to the initial positive rotation are plotted as ordinates against the concentration of the acid as abscissæ. In Curve A the concentration is expressed in terms of the number of molecular proportions of hydrone to one of acid, and in Curve B as the number of molecular proportions of acid to 300 of hydrone.

Curve B is a straight line. The ratio of the rotation produced by the invert sugar to that of the original cane sugar in the absence of acid can be deduced by extrapolation to zero concentration of acid.

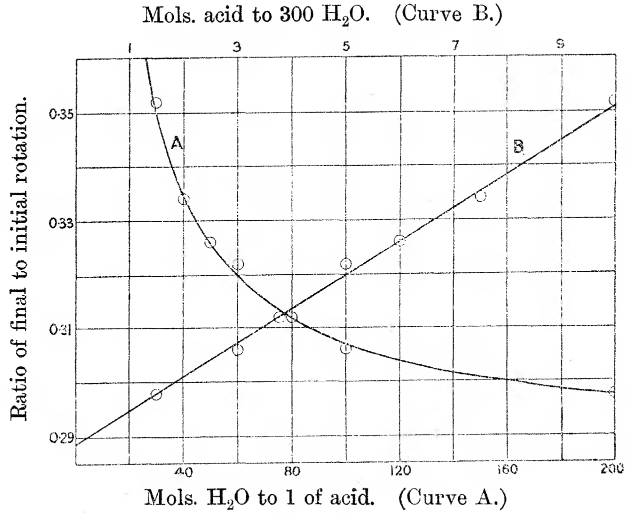

DIAGRAM I.

In the experiments carried out to find the effect of acid on the rotatory power of cane sugar, glucose and fructose, the molecular proportions used were very approximately 0·25 of sugar and 40 of hydrone in the presence and absence of 1 of benzenesulphonic acid.

The cane sugar used was carefully purified coffee sugar, specially supplied by Messrs. Tate and Sons. Kahlbaum's first quality glucose and "crystallised" fructose were used. The water of crystallisation of the glucose was removed by desiccation *in vacuo* over concentrated sulphuric acid at 102° C. No special precautions were taken to purify the glucose and fructose, as the object of the experiments was to find the *change* in rotatory power caused by the presence of the acid; judging from the rotatory powers arrived at, however, it is evident that there was little impurity present. The chief essential was that the samples used in the experiments with and without acid should not differ in rotatory power; to ensure this, a weighed quantity of the sugar was dissolved in water and portions of this solution were used in making up the solutions for the experiments. Care was taken that mutarotation was always complete. The same polarimeter tube was used throughout.

In order to deduce the value of the initial rotatory power of the cane sugar in the presence of the acid, it was necessary to make observations as soon after mixing as possible and by extrapolation to deduce the value of the rotation produced at the time of mixing. The solutions were contained unmixed in the mixing apparatus, described in Part XII, consisting of two 100 c.c. Jena conical flasks connected by a short wide U-tube ground into the necks. After being brought to 25° C. in the constant temperature air chamber described in Part XXII, the solutions were quickly mixed while still in the chamber, the time being noted; they were then immediately transferred to the polarimeter tube which was already at 25° on the water circuit. Readings of the rotatory power were taken at half-minute intervals and from these it was easy to find with a close approach to accuracy by extrapolation the value of the rotatory power at the time of mixing. The initial rotatory powers given above were obtained in this manner.

Table II.

Time in minutes after mixing	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0
Rotation	29·06	28·71	28·42	28·14	27·83	27·52	27·18	26·88

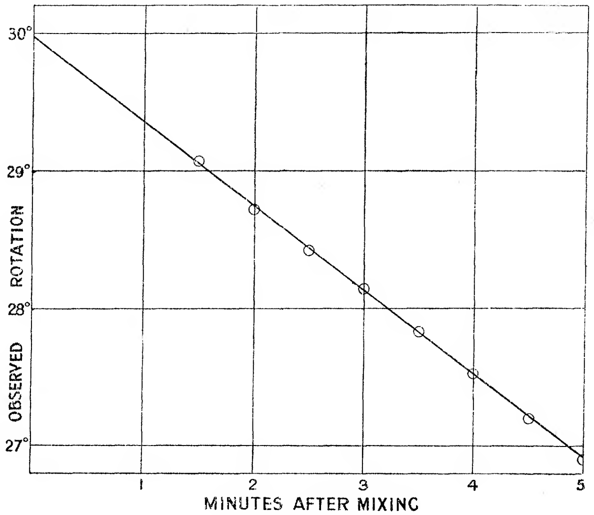

DIAGRAM II.

The data in Table II, which are shown graphically in Diagram II, are derived from the experiment carried out to determine the rotatory power of cane sugar in the presence of benzenesulphonic acid and indicate the degree of accuracy of the method of finding the initial rotation by extrapolation.

Table III contains the experimental data and the deduced specific rotatory powers of cane sugar, glucose and fructose, in the presence and absence of benzene-sulphonic acid. The molecular proportions used were 0·25 of sugar, 40 of water and 1 of acid.

Table III.

	Observed rotation.	Density of solution.	Grm. of sugar per grm. of sol.	$[\alpha]^{25}_{\mathrm{Hg}}$.
Cane sugar alone ...	+34°·505	1·03906	0·10605	+78°·28
„ +acid	+29°·96	1·09429	0·08867	+77°·19
				Diff. 1°·09
Glucose alone	+14°·96	1·01961	0·05874	+62°·45
„ +acid......	+12°·885	1·07903	0·04871	+61°·29
				Diff. 1°·16
Fructose alone	−25°·02	1·02002	0·05874	−104°·40
„ +acid ...	−22°·84	1·07937	0·04873	−108°·56
				Diff. 4°·16

It will be observed that the change in specific rotatory power caused by the acid is in the same direction in the case of all three sugars, viz., a decrease in positive or an increase in negative rotation, the change being considerably greater in the case of fructose than in that of cane sugar or glucose. Moreover, in each case, the change would increase the value of the ratio of the final negative rotation of the invert sugar to the initial positive rotation of the cane sugar in the experiments described above. Furthermore, omitting in each case any mutual effect that glucose and fructose may have on their individual specific rotatory powers, the specific rotatory power of invert sugar in the absence and presence respectively of acid would be

$$\frac{62{\cdot}45-104{\cdot}40}{2}\,(=20{\cdot}975) \quad \text{and} \quad \frac{61{\cdot}59-108{\cdot}56}{2}\,(=23{\cdot}635).$$

The value of the ratio found when the molecular proportion of water to acid was 40 to 1 was 0·334. In the absence of acid, therefore, it should be

$$\frac{0{\cdot}334}{1}\times\frac{77{\cdot}19}{78{\cdot}28}\times\frac{20{\cdot}975}{23{\cdot}635}=0{\cdot}292.$$

This value is practically identical with that found from Diagram I by extrapolation to zero concentration of acid, viz., 0·289; that found when sulphuric acid is used is 0·290.

It is therefore clear that the large alteration produced by the acid in the value of the ratio of the final to the initial rotation in the experiments on the hydrolysis of cane sugar can be completely and satisfactorily explained by the changes produced by the acid in the rotatory powers of the three sugars involved.

The Decrease in Velocity of α-Particles in Passing through Matter.

By E. Marsden, M.Sc., Lecturer, and T. S. Taylor, Ph.D., John Harling Fellow, University of Manchester.

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It is becoming recognised that one of the most fruitful sources of information as to the internal structure of atoms is provided by the phenomena attending the passage of swift electrified particles through them. In particular from a consideration of the scattering of α-particles it has been found that the atom consists essentially of a very concentrated charge at the centre of the atom* surrounded by electricity of the opposite sign, probably electrons, distributed throughout the remainder of the atom. Further, Darwin† and Bohr‡ have attempted to obtain information as to the number and distribution of electrons in the atom by a consideration of the absorption or loss of velocity of the α-particles in passing through matter. The only data for this purpose so far obtainable are provided by the velocity curves, or relations between velocity and thickness of matter traversed, in aluminium as determined by Rutherford,§ and in mica as determined by Geiger.|| It seemed, therefore, of interest to make a more complete investigation of the velocity curves in various substances, more particularly as the earlier observations are subject to slight errors due to the assumption that equal thicknesses of matter have the same air equivalent at different parts of the range of α-particles.

In the present experiments the velocity curves in gold, copper, aluminium, mica and air have been determined, using as source the α-particles of

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* E. Rutherford, 'Phil. Mag.,' 1911, vol. 21, p. 669.

† C. G. Darwin, 'Phil. Mag.,' 1912, vol. 23, p. 907.

‡ N. Bohr, 'Phil. Mag.,' 1913, vol. 25, p. 10.

§ E. Rutherford, 'Phil. Mag.,' 1906, vol. 12, p. 138.

|| Geiger, 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 505.